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(19) Japanese Patent Office (JP)

(12) **Laid Open Patent Application Gazette (A)**

(11) Laid Open Patent Application Number H10-152575

(43) Publication Date: 9th June 1998

(51) Int. Cl[6]	File No.	FI
C 08 J 9/32		C 08 J 9/32
B 29 C 45/00		B 29 C 45/00
47/00		47/00
//B 29 K 101:12		
105:04		

Request for Examination: Not yet requested

Type of Application: FD

Number of Claims: One

Number of Pages in the Japanese Text: Five

(21) Application Number: H8-327728

(22) Date of Application: 22nd November 1996

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(54) Title of the Invention: A method for the foaming and moulding of thermoplastic resins

(57)

Abstract

Problem:

To provide a method for the foaming and moulding by extrusion or injection moulding of a thermoplastic resin with which it is possible to realise a fine and uniform dense foamed state and a beautiful surface, and

with which foaming can be carried out to a target density.

Means of Resolution:

Thermally expandable microcapsules are mixed with the thermoplastic resin raw material and the thermally expandable microcapsules are expanded by the milling and melting heat and the mixture is foamed and moulded by extrusion moulding or injection moulding. In this way it is possible to achieve stable foaming in a state where a microcapsule is enveloped in each pore, to achieve a fine and uniform dense foamed state, to provide a beautiful surface, and to carry out foaming to a target density.

Scope of the Patent Claims

[Claim 1]

A method for the foaming and moulding by extrusion or injection moulding of a thermoplastic resin, characterised in that thermally expandable microcapsules are mixed with the thermoplastic resin raw material and the said thermally expandable microcapsules are expanded by the milling and melting heat as the mixture is moulded by extrusion moulding or injection moulding.

Detailed Description of the Invention

[0001]

<u>Technical Field of the Invention</u>

The invention concerns a method for the foaming and moulding of a thermoplastic resin by extrusion moulding or injection moulding, being a method of moulding with which uniform and dense foaming can be achieved.

[0002]

<u>Prior Art</u>

Foaming and moulding using a thermoplastic resin is carried out for moulding a variety of synthetic resin products, and it is used to reduce the weight and to improve the thermal insulation properties of synthetic resin products, and to provide products with cushioning properties, by foaming.

[0003]

Examples of the usual methods of foaming and moulding with thermoplastic resins of this type include the methods where a chemical foaming agent is mixed with the thermoplastic resin raw material and the chemical foaming agent is thermally degraded by the heat on melting the thermoplastic resin raw material to produce a gas, and the methods in which steam or a gas

such as nitrogen or carbon dioxide is introduced into the melted thermoplastic resin.

[0004]

Problems to be Resolved by the Invention

With the methods for the foaming and moulding of thermoplastic resins of this type, the foaming and moulding is carried out with the thermal degradation gas or the gas which has been introduced in a state where the thermoplastic resin raw material has been melted and the viscosity has been greatly reduced, and the state of the pores varies greatly as a result of small pressure variations in the thermal degradation gas or the gas which has been introduced and it is difficult to obtain a uniform and dense moulding, and there is a further problem in that gas is also likely to escape from the system so that it is difficult to obtain a product which has the target density as a stable foamed state.

[0005]

Furthermore, when extrusion moulding with thermoplastic resins there is a sudden fall pressure when the resin in a foamed state passes through the die and so the gas expands further and, as a result of this, there is a problem in that fine bulges and hollows are produced on the surface of the moulding and a rough "orange peel" effect is produced and it is impossible to obtain a beautiful surface.

[0006]

The present invention is based upon an understanding of these problems with the prior art and it is intended to provide a method for the foaming and moulding by means of the extrusion or injection of thermoplastic resins with which a fine and uniform dense foamed state can be realised, with which a

beautiful surface can be obtained, and with which the material can be foamed to the target density.

[0007]

Means of Resolving These Problems

In order to resolve the above mentioned problems of the prior art, the present invention is based upon the fact that it is difficult to control the dispersion of the gas and to form pores of a fixed diameter with the methods where a gas is dispersed directly in a molten resin of the prior art, and in practical terms it is a method for the foaming and moulding of a thermoplastic resin by means of extrusion moulding or injection moulding which is characterised in that thermally expandable microcapsules are mixed with the thermoplastic resin raw material and the said thermally expandable microcapsules are expanded by the milling and melting heat and the mixture is foamed and moulded by extrusion moulding or injection moulding.

[0008]

According to this method for the foaming and moulding of a thermoplastic resin, thermally expandable microcapsules are mixed with the thermoplastic resin and the thermally expandable microcapsules are caused to expand by the milling and melting heat and the mixture is foamed and moulded by extrusion moulding or injection moulding and each pore is blown in a stable manner by means of a microcapsule, and it is possible to realise a fine and uniform dense foamed state and a beautiful surface and it is also possible to carry out foaming to the target density.

[0009]

Here resins such as PVC (poly(vinyl chloride)), PS (polystyrene), PP (polypropylene), PPO, PE (polyethylene) and the like which are generally known

as thermoplastic resins; PBT (poly)butylene terephthalate)), nylon, PC (polycarbonate), PET (poly(ethylene terephthalate)) and the like which are generally known as engineering plastics; and EEA (ethylene/ethyl acrylate copolymer), AAS (acrylonitrile/acrylate/styrene copolymer), EVA (ethylene/vinyl acetate copolymer), TPU (thermoplastic urethane elastomer), TPEE (thermoplastic ester elastomer) and the like which are generally known as elastomers can be cited as examples of the thermoplastic resin, and other materials such as lubricants, plasticizers, antioxidants and the like can be added to these resins as auxiliary agents.

[0010]

The thermally expandable microcapsules are microcapsules where a liquid or gas which expands on heating is enclosed in a synthetic resin capsule and the microcapsule which forms the outer shell is caused to expand by the expansion of the liquid or gas which is enclosed therein by the milling and melting heat generated by the screw etc. at the time of extrusion moulding or injection moulding, and the moulding is completed without the microcapsules being melted or bursting under the temperature conditions imposed during moulding.

[0011]

Copolymers which have acrylonitrile as one of the monomer components can be used for the microcapsule material, and other monomer components which may be used for copolymerisation with the acrylonitrile include, for example, acrylic acid, methacrylic acid, acrylic acid esters, methacrylic acid esters, styrene, vinyl acetate and vinylidene chloride, but there is no limitation to just these monomers.

[0012]

Liquids which form gases at temperatures below the softening point of the microcapsules and expand can be used for the liquid or gas which is enclosed in the microcapsules and, for example, low boiling point liquids such as propane, propylene, butene, n-butane, isobutane, isopentane, neopentane, n-pentane, hexane, heptane, petroleum ether, halogenated compounds such as methyl chloride and methylene chloride, chlorofluorocarbons such as CCl_3F and CCl_2F_2, and tetra-alkylsilanes such as tetramethylsilane and trimethylethylsilane, as well as compounds which are thermally degraded by heat and form a gas, such as AIBN, for example, can be used as the liquids or gases which are enclosed in the microcapsules.

[0013]

Embodiment of the Invention

An embodiment of the invention is described in detail below. In those cases where, in the method for the foaming and moulding of a thermoplastic resin of this invention, extrusion moulding or injection moulding is carried out using a thermoplastic resin, the thermoplastic resin raw material and thermally expandable microcapsules are introduced into the hopper at the same time and mixed together and the thermoplastic resin and the thermally expandable microcapsules are introduced under pressure in the form of a mixture into the die or mould with an extruding machine or an injection machine and foaming and moulding are carried out.

[0014]

On extrusion moulding or injection moulding, the outer shells of the microcapsules which are made of synthetic resin are softened when the raw material

thermoplastic resin is being heated and melted and the gas or liquid which is contained within the microcapsules is also heated and formed into a gas and expanded, the outer synthetic resin shells are pushed out and expanded, and in this way a foamed state is obtained.

[0015]

Hence, the outer shells of the thermally expandable microcapsules must have temperature characteristics such that they soften but do not melt under the moulding temperature conditions of the raw material thermoplastic resin, and the aforementioned thermally expandable microcapsules and the temperature conditions are selected appropriately in accordance with the type of thermoplastic resin indicated earlier, and the low boiling point liquid, for example, which is included in the microcapsules can be selected for use from among those mentioned above which form a gas at the melting temperature of the thermoplastic resin raw material.

[0016]

Furthermore, on extrusion moulding or injection moulding, the raw material which has been introduced from the hopper is milled with a screw, for example, in the extruding machine or injecting machine and shear forces are imposed on the thermally expandable microcapsules by the milling, and extruding forces or injecting forces are also imposed when the material is being pushed through the die or into the mould, and the microcapsules selected must not fail even when these forces are being applied, and the size of the microcapsules can be selected.

[0017]

With extrusion moulding or injection moulding of

this type, foams can be moulded in a state where the thermally expandable microcapsules have expanded and are included in the thermoplastic resin and each pore is stable in a state where it envelops a microcapsule, and in the case of extrusion moulding there is no direct leakage of gas from the moulded product in the state where the material has been extruded from the die and the pressure has been released and it is possible to obtain a foam of which the surface has a good appearance.

[0018]

Now, the number and size of the pores is determined by the number of thermally expandable microcapsules introduced (amount admixed) and their size after expansion in a foam moulding which has been moulded by extrusion moulding or injection moulding in this way, and since the density of the moulding is determined by these factors it is possible to control the foamed state by means of the number of unexpanded expandable microcapsules which are mixed with the thermoplastic resin (amount admixed) and the predicted size of the thermally expandable microcapsules after they have been caused to expand by the heat during the course of moulding, and since there is virtually no leakage of gas from the system when compared with the case where a gas is caused to expand directly as in the past, and it is possible to realise a target density quite easily.

[0019]

Thus, when low weight and thermal insulating properties are required for a construction material, for example, this can be achieved by admixing a large number of comparatively large thermally expandable microcapsules.

[0020]

Furthermore, in those cases where a uniform dense foamed state is required, as in the case of the foam rollers used in office machines, for example, a uniform dense moulding can be obtained using very small spherical expandable microcapsules, which have a diameter of from 5 to 30 μm and provide a diameter after expansion of from 10 to 100 μm, in admixture with the thermoplastic resin.

[0021]

Moreover, when a foam which has a cushioning effect and which is impermeable to water, such as a shoe sole sponge for example, is required, the pores are formed with thermally expandable microcapsules and so they are isolated pores and the material is impermeable to water, and the required cushioning properties can be achieved by controlling the size and number of pores.

[0022]

Illustrative Examples

Examples and comparative examples of the invention are described below.

[0023]

Example 1

Extrusion moulding was carried out using a thermoplastic urethane elastomer for the thermoplastic resin with varying amounts of thermally expandable microcapsules to provide four types of extrusion moulding (Examples A to D).

[0024]

Furthermore, foam extrusion moulding was carried out by adding a chemical foaming agent to the same thermoplastic resin raw material as a comparative example.

[0025]

The resin used was a thermoplastic urethane elastomer (TPU) (manufactured by Nippon Mirakutoran).

[0026]

Microcapsules with the trade name "Expancel" (manufactured by Nippon Firaito) were used for the thermally expandable microcapsules. The shells of these thermally expandable microcapsules comprised vinylidene chloride/acrylonitrile copolymer and the enclosed gas was isobutane, and the properties before and after expansion of these thermally expandable microcapsules were as shown in Table 1.

[0027]

The thermally expandable microcapsules were compounded in each of four amounts, namely 1.5, 3, 5 and 10 parts (by weight, same hereinafter), per 100 parts of the thermoplastic resin.

[0028]

The chemical foaming agent used in the comparative example was azodicarboxamide. Various auxiliary agents were added as well.

[0029]

The densities of the foam mouldings obtained in this way were measured and the surface appearances and the cell structures in the cross section were observed, and the results obtained are shown in Table 2.

[0030]

Table 1

	Unexpanded	After Expansion
Average Particle Diameter (μm)	10 - 16	40 - 60
Particle Diameter Range (μm)	5 - 30	10 - 100
Bulk Density (g/cm²)	0.7	Less than 0.02
True Density (g/cm²)	1.3	Less than 0.04
Expansion Temperature (°C)	80 - 150	
Colour	Light yellow or white	White
Resistance to Styrene and Other Solvents	Good	Good

[0031]

Table 2

	Example A	Example B	Example C	Example D	Comp. Ex.
TPU	100	100	100	100	100
Expancel	1.5	3	5	10	
Azodicarboxamide					1.5
Die Temp. °C	160	160	160	160	160
Density (g/cm^3)	0.77	0.72	0.52	0.42	0.75
Surface Appearance	Good	Good	Good	Good	Poor, Rough
Cell Structure in the Cross Section	Uniform	Uniform	Uniform	Uniform	Irregular

[0032]

It is clear from this table that the surface appearance was good and not rough, and that the cell structure of the cross section was uniform in the foam mouldings obtained by extrusion moulding using thermally expandable microcapsules of this invention.

[0033]

Furthermore, it was confirmed that the density of the foamed moulding varied in accordance with the amount of thermally expandable microcapsules compounded.

[0034]

Example 2

Extrusion moulding was carried out using vinyl chloride for the thermoplastic elastomer and varying the amount of thermally expandable microcapsules compounded and three types of moulding were obtained (Examples A to C).

[0035]

Furthermore, foam extrusion moulding was carried out by adding a chemical foaming agent to the same thermoplastic resin raw material as a comparative example.

[0036]

Vinyl chloride which had a degree of polymerisation of 800 was used for the resin, and to this had been added 0.5 part of lead stearate as a lead-based stabiliser.

[0037]

The same microcapsules as in Example 1, which is to say microcapsules of trade name "Expancel" (manufactured by Nippon Firaito), were used for the thermally expandable microcapsules.

[0038]

The thermally expandable microcapsules were compounded in each of three amounts, namely 1.5, 3 and 10 parts, per 100 parts of the thermoplastic resin.

[0039]

The chemical foaming agent used in the comparative example was azodicarboxamide.

[0040]

Moreover 0.5 part of calcium stearate was added as a lubricant and various auxiliary agents such as filler and pigment, for example, were also added.

[0041]

The densities of the foam mouldings obtained in this way were measured and the surface appearances and the cell structures in the cross section were observed, and the results obtained are shown in Table 3.

[0042]

Table 3

	Example A	Example B	Example C	Comp. Ex.
PVC	100	100	100	100
Lead Stearate	0.5	0.5	0.5	0.5
Calcium Stearate	0.5	0.5	0.5	0.5
Calcium Carbonate	10	10	10	10
Pigment	0.5	0.5	0.5	0.5
Expancel	1.5	3	10	
Azodicarboxamide				1.5
Density (g/cm^3)	0.75	0.70	0.48	0.65
Surface Appearance	Good	Good	Good	Poor, Rough
Cell Structure in the Cross Section	Uniform	Uniform	Uniform	Irregular

[0043]

It is clear from this table that the surface appearance was good and not rough and that the cell structure of the cross section was uniform in the foam mouldings obtained by extrusion moulding using thermally expandable microcapsules of this invention.

[0044]

Furthermore, it was confirmed that the density of the foamed moulding varied in accordance with the amount of thermally expandable microcapsules compounded.

[0045]

Moreover, cases where the amount of thermally expandable microcapsules compounded has been set to from 1.5 to 10 parts per 100 parts of thermoplastic resin raw material have been described in Examples 1 and 2 above, but the amount compounded can be varied appropriately in accordance with the foam moulding

density required, and it is not limited to the amounts shown in Examples 1 and 2.

[0046]

Effect of the Invention

As described in practical terms in the embodiments above, with the method for the foaming and moulding of a thermoplastic resin of this invention, thermally expandable microcapsules are mixed with the thermoplastic resin and the thermally expandable microcapsules are caused to expand by the milling and melting heat and foaming and moulding is carried out by extrusion moulding or injection moulding, and so foaming where each pore is stable is achieved with the microcapsules and it is possible to achieve foaming with a fine and uniform dense foamed state, with which a beautiful surface is obtained, and with which foaming can be carried out to provide a target density.

[0047]

By this means it is possible to obtain easily foam mouldings which have the uniform dense pore and surface characteristics required for paper feed with a foam roller as used in office machines, to provide excellent thermal insulation characteristics with light weight for construction materials, and to provide characteristics of water impermeability while having cushioning properties as in the case of a sponge which is used for a shoe sole for example.